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NEW HYPOFLUORITES CONTAINING NITROGEN

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Technical Summary Report

I. Fluorination of CF_3NO and reactions of its fluorination products.

The fluorination study of trifluoronitromethane in the presence of a AgF_2 catalyst (as described in earlier reports) has now been completed.

3.7 grams of 100% CF_3NO was fluorinated as it was carried by nitrogen (2 l/hr) and contacted with fluorine (1 l hr) just before entering the AgF_2 catalytic reactor. The residence time was roughly 10 minutes at 125°. The compounds and yields obtained based on CF_3NO consumed are as follows:

Compound	%	Compound	%
$(\text{CF}_3)_2\text{NOCPF}_3$	17.3	CF_4	23.0
	0.5	C_2F_6	14.2
NF	4.7	NF_3	5.5
CF_3N	2.0	COF_2	3.7 mM

Silicon tetrafluoride was found in very small amounts.

Equimolar amounts of CF_3NO and F_2 were condensed into a quartz tube and allowed to warm to room temperature. Upon initiation of UV radiation, a flash occurred in the tube. Radiation was continued for 30 minutes. Separation of the reaction products indicated the presence of SiF_4 , NO_2 , COF_2 , CF_4 , NF_3 , $(\text{CF}_3)_2\text{NF}$ and $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$.

Continuing the characterization of $(\text{CF}_3)_2\text{NOCPF}_3$, 1.9 mM (0.46g) of the compound (95% pure) was condensed into an ampoule (70 ml. volume) which contained 0.7 g KI dissolved in 0.5 ml of water + 25 ml. of acetonitrile. The ampoule was agitated for four days at room temperature and for several hours at 30°. Although some color developed in the tube, indicating oxidation of the iodide ion, when the gaseous materials were passed through a trap at -23° and a trap at -183°, no evidence for decomposition of the $(\text{CF}_3)_2\text{NOCPF}_3$ was found.

Earlier we have shown that the compound $(CF_3)_2NOCP_3$ apparently has considerable stability toward fluorination even at 200° in the presence of N_2 . Pyrolysis was attempted by holding 0.45 mM of the compound in a Monel tube at 350° for 30 minutes. An infrared spectrum indicated no decomposition had occurred. The material was returned to the Monel tube and maintained at 440° for 45 minutes. Less than 10% decomposition occurred. Products have not been identified.

II. Photolysis reaction of carbon monoxide and tetrafluorohydrazine.
Photolysis reaction of oxalyl chloride and tetrafluorohydrazine.
Characterization of reaction products.

Conditions of concentration, time of irradiation, and other experimental conditions were varied in an attempt to obtain as high a yield of NF_2COF as possible from the irradiation of CO and N_2F_4 . Yields as high as 13% (3.5mM) based on 26 mM N_2F_4 were obtained when a mixture composed of 150 mM N_2F_4 and 200 mM CO in a 3.2 liter Pyrex bulb with a quartz inset was irradiated for approximately three hours. Other products usually obtained are: N_2O , COF_2 , N_2F_2 and CO_2 . Purification of the NF_2COF is best brought about through the use of an unpacked twelve foot coiled copper column (1/8" i.d.) in a fractional codistillation apparatus. However, some difficulty is encountered in trying to separate the NF_2COF from difluoroamine which apparently is a hydrolysis product. Attempts are currently being made to obtain a more nearly anhydrous system.

The infrared spectrum consists of 6 bands including those at 1860, 1210, 1040, 960, 835 and 770 cm^{-1} . All of these are strong except the one at 835 cm^{-1} which is very weak at 10-15 mm pressure in a 5 cm cell. Molecular weight determinations fall in the range between 90 and 102.5. The mass

spectrum includes a parent peak at m/e = 99 and the nuclear magnetic resonance spectrum shows the presence of a NF_2 -fluorine resonance and a C-F-fluorine resonance. Peak areas are approximately in the ratio 2:1 ($\text{NF}_2:\text{CF}$). Chemical shifts relative to CCl_3F are N-F, -33 ppm and C-F, +11 ppm. The NF_2 chemical shift is small compared to the usual but there is a dearth of information on chemical shifts for N-F compounds. Vapor pressure determination on a single sample which is probably 97 - 98% NF_2COF indicates a boiling point of about -46°C whereas Ruff and Giese (Berichte, 69, 684 (1936)) indicated a boiling point of -82° for the compound which they suggested was NF_2ClF . From this vapor pressure data, the heat of vaporization is approximately 2600 kcal/mole. It should be emphasized that these data are only approximate because of the impurity of the material. Hopefully, work on this compound will soon be finished. A low temperature fluorination is also planned.

Vapor phase reactions of oxalyl chloride and tetrafluorohydrazine were run under a variety of conditions in an attempt to find a simple preparation of NF_2COCl .

1. Two hundred mm of roughly equimolar mixture of N_2F_4 and $(\text{COCl})_2$, in a Pyrex bulb at room temperature for ten minutes and at 40° for ten hours, did not react. This mixture at about one atmosphere pressure was heated in a Monel tube at 100° for 24 hours yielded some noncondensable (probably CO), trace of COF_2 , COCl_2 , some COClF and N_2F_2 .
2. Mixtures of N_2F_4 and $(\text{COCl})_2$ irradiated with UV in a small quartz tube for about 30 minutes gave large amounts of COClF , some COCl_2 , a trace of COF_2 and CO. However, pure oxalyl chloride irradiated under the same conditions is completely decomposed into COCl_2 , Cl_2 and CO.

3. Irradiation of a N_2F_4 - $(COCl)_2$ in a 200 ml. Pyrex bulb for 1.5 hours resulted only in partial decomposition of the chloride to $COCl_2$, and recovery of N_2F_4 . It appears that the formation of NF_2COCl at ambient temperature is essentially precluded because of the low stability of the N-C bond. If this compound is present, the yield must be very low. Work is continuing here.

III. Reactions of N_2F_4 or F_2 with perfluoroacetyl compounds.

→ In a continuation of attempts toward the preparation of nitrogen-containing hypofluorites, preparation of some perfluoro compounds which could be used as starting materials have been investigated. ←

1. Fluorination of CF_3CONH_2 in static and flow reactors with fluorine diluted by nitrogen at temperatures ranging between -78° and room temperature resulted in the production of the following products: CF_3COF , COF_2 , CF_4 , NF_3 , and other products. Less harsh conditions are indicated if the desired compound, CF_3CONF_2 , is to be obtained.

2. When a mixture consisting of N_2F_4 (20 mm) and CF_3COBr (32 mm) was diluted to a total pressure of 140 mm with dry nitrogen, no reaction occurred at room temperature on prolonged standing. When a similar mixture, without nitrogen, was subjected to UV irradiation in a quartz vessel for 40 minutes, reaction did occur and some of the products have been identified as SiF_4 , CF_3COF , CF_3NF_2 , CF_3Br and Br_2 . Work is continuing here.